

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-085821

(43)Date of publication of application : 06.04.1993

(51)Int.Cl.

C04B 35/50

C04B 35/10

(21)Application number : 03-273601

(71)Applicant : OMORI MAMORU

(22)Date of filing : 26.09.1991

(72)Inventor : OMORI MAMORU
HIRAI TOSHIO

(54) SINTERED RARE-EARTH METAL OXIDE-ALUMINA AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain the subject sintered compact having excellent strength and toughness and suitable for practical use by specifying the baking temperature and the baking time of a mixture of a rare-earth metal oxide and alumina, thereby decreasing the crystal particle diameter of the sintered product below a prescribed level.

CONSTITUTION: The objective rare-earth oxide-alumina sintered compact having crystal particle diameter of $\leq 30\mu\text{m}$ and free from the generation of defects such as void and pore and the abnormal particle growth causing the lowering of strength and toughness can be produced by forming a mixture of 5-95wt.% of rare-earth metal oxide such as Sc_2O_3 , Y_2O_3 and La_2O_3 and 5-95wt.% of alumina, heating the mixture at a heating rate of 1-200°C/min and keeping at 1500-1800°C for 0.1-10hr. The sintered compact is e.g. composed mainly of $\text{Ln}_4\text{Al}_2\text{O}_9$ or LnAlO_3 (Ln is rare-earth element or their mixture).

LEGAL STATUS

[Date of request for examination] 26.02.1998

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3007730

[Date of registration] 26.11.1999

[Number of appeal against examiner's decision of

rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention is proposed about a precise rare earth oxide-alumina sintered compact on an organization target with high reinforcement and high toughness by lessening pore in the ceramics leading to reinforcement or a toughness fall about a rare earth oxide-alumina sintered compact and its manufacture approach, and controlling abnormality grain growth.

[0002]

[Description of the Prior Art] The oxide system ceramics has the high reinforcement in an elevated temperature, and since it excels in thermal resistance, oxidation resistance, and corrosion resistance, the temperature of hundreds of or less times of the melting point can trust and use it at least. So, promising ** of the rare earth oxide (the rare earth elements and oxide of those mixture) and alumina with which the melting point exceeds 2000 degrees C was carried out as a high-temperature-service ceramic ingredient. The case of the mixed ceramics which consists of two kinds of this oxide especially is also about 2000 degrees C, and that melting point is considered to be an effective thing as the so-called high temperature materials.

[0003] However, since crystal grain caused abnormality growth and served as a big diameter of crystal grain of 100 micrometers or more in case the mixture of an oxide is calcinated and a sintered compact is generally obtained about the oxide mixing ceramics, there was a problem that eburnation was hard to be carried out that pore is easy to be formed. And the sintered compact obtained became only what has them for the crystal grain which carried out abnormality growth, or said pore. [remarkable reinforcement, toughness, and a degree of hardness and small] In such a reason, by the time practical use was presented with the sintered compact of such oxide mixing ceramics, it did not result till today.

[0004] In order that a rare earth oxide might generate twin crystal by the martensitic transformation in the case of baking especially about Ln₄aluminum 2O₉ or the compound of a presentation which becomes LnAlO₃, there was a fatal fault that only a very weak polycrystal sintered compact could be obtained.

[0005]

[Problem(s) to be Solved by the Invention] By the way, as an approach of controlling abnormality grain growth of the polycrystal sintered compact of the oxide mixing ceramics mentioned above, the approach of controlling burning temperature and firing time was conventionally considered to be effective vaguely. However, since, as for the sintered compact of a rare earth oxide-alumina system, said control technique is not yet established, the actual condition is not put in practical use as a ceramic ingredient.

[0006] The purpose of this invention is to propose the rare earth oxide-alumina sintered compact suitable for practical use in which studied the burning temperature of that, and the suitable conditions of firing time, controlled and had the diameter of crystal grain of this sintered compact in fitness by this about establishing said control technique with repetitive possibility, i.e., the polycrystal sintered compact of the oxide mixing ceramics, and both reinforcement and toughness were excellent, and its manufacture approach.

[0007]

[Means for Solving the Problem] In order to realize the purpose of upper **, as a result of inquiring wholeheartedly, when artificers controlled the diameter of crystal grain of the mixture sintered compact of a rare earth oxide and an alumina to 30 micrometers or less, it traced that the desired reinforcement and the desired toughness which this kind of sintered compact is expected were acquired. Then, about the conditions for obtaining such a diameter of crystal grain, when inquired further, performing baking which makes burning temperature within the limits of 1500-1800 degrees C, and makes firing time 0.1 - 10 hours under the predetermined blending ratio of

coal acquired the knowledge of being effective, and it completed this invention of the following summary configurations.

[0008] This invention namely, mixture (rare earth oxide 5 - 95wt% and alumina 95 - 5wt%) The manufacture approach of the rare earth oxide-alumina sintered compact characterized by heating this mixture with the programming rate for 1 - 200 **/after that, and calcinating by fabricating and holding in a 1500-1800-degree C temperature region for 0.1 to 10 hours, The rare earth oxide-alumina sintered compact whose diameter of crystal grain compounded by it is 30 micrometers or less, And the manufacture approach of a rare earth oxide-alumina sintered compact that said rare earth oxide-alumina sintered compact is what uses Ln₄aluminum 2O₉ or LnAlO₃ as a principal component, and the diameter of crystal grain compounded by it are the rare earth oxide-alumina sintered compacts which are 30 micrometers or less.

[0009]

[Function] According to the place as for which artificers did knowledge, it is important for a rare earth oxide-alumina sintered compact to control the particle size of the constituent particle to 30 micrometers or less, and he has noticed control of such a diameter of crystal grain being attained by devising baking conditions. Then, as a result of advancing and doing research further, it hit on an idea of being effective in the pore in the sintered compact with which performing proper both combination and sintering of proper burning temperature and fitness firing time causes reinforcement and a toughness fall, or prevention of abnormality grain growth to a header and this invention.

[0010] According to the manufacture approach of the rare earth oxide-alumina sintered compact of this invention, it is rare earth oxide powder first. 5 - 95wt% and alumina powder 95 - 5wt% are mixed.

[0011] Here, the property of a rare earth oxide-alumina system sintered compact that rare earth oxide powder is obtained less than [5wt%] became what inclined toward the alumina sintered compact independent property, and since an alumina became that from which the property of the rare earth oxide-alumina sintered compact obtained inclined toward the rare earth oxide independent property less than [5wt%] on the other hand, it limited to the above-mentioned range.

[0012] In addition, it is a rare earth oxide (Ln 2O₃), For example, Sc 2O₃, Y₂O₃, La 2O₃, CeO₂ and Pr 2O₃, Nd 2O₃, Sm 2O₃, Eu₂O₃, Gd 2O₃, Tb 2O₃, Dy 2O₃, Ho 2O₃, Er 2O₃, Tm 2O₃, Yb 2O₃, and Lu 2O₃ are used suitably.

[0013] Moreover, in mixing of said oxide powder, the usual machine used for mixing or kneading of fine particles can be used. Either dry type or wet are OK as this mixing, and in especially a wet case, it is effectively mixable if surface active agents, such as ethylamine and fish oil, are used.

[0014] Next, it once dries and the mixed raw material obtained as mentioned above is succeedingly fabricated in the generation form of a predetermined configuration. As a shaping assistant, it can add in the above-mentioned mixed raw material, and organic giant molecules (a polyethylene glycol, polyvinyl alcohol, etc.) can be fabricated in this forming cycle with the application of the known forming technique of a conventional method.

[0015] Next, said generation form is heated with the programming rate of 1 - 200 **, and let it be a sintered compact by baking processing held in temperature of 1500-1800 degrees C for 0.1 to 10 hours. A sintered compact precise [when this burning temperature is lower than 1500 degrees C] since sintering becomes inadequate cannot be obtained, but on the other hand, if higher than 1800 degrees C, abnormality growth of crystal grain will be caused. The range of fitness burning temperature is limited to the range of 1500-1800 degrees C from this. Next, firing time is 0.1 although it is desirable to make it short when high for a long time [when burning temperature is low] in relation to said burning temperature. When shorter than time amount, since sintering was inadequate, a precise sintered compact could not be obtained, but on the other hand, in order to cause abnormality growth of crystal grain by ** for 10 hours, it limited to the range of 0.1 - 10 hours. Moreover, if a programming rate is slower than a part for 1-degree-C/, it takes [sintering] time amount too much and is not economical, and on the other hand, since a precise sintered compact will not be obtained if quicker than a part for 200 **/, it is limited to the range of 1 - 200 **.

[0016] In addition, as an ambient atmosphere at the time of baking, although an oxidizing atmosphere is desirable, a non-oxidizing atmosphere (for example, nitrogen gas, argon gas, gaseous helium) is sufficient, and you may calcinate in a vacuum further.

[0017] As for the rare earth oxide-alumina system sintered compact obtained with the application of such baking conditions, the diameter of crystal grain of a constituent particle is controlled by 30 micrometers or less. Consequently, in the former, the rare earth oxide-alumina sintered compact which has the reinforcement which was not able to be expected, and a toughness value can be obtained.

[0018] Generally, if the diameter of crystal grain of a constituent particle exceeds 50 micrometers, as for the ceramics, a strong fall will become remarkable. Therefore, particle size must be set to 50 micrometers or less in order to obtain the ceramic ingredient of high intensity. So, if mean particle diameter is set to 30 micrometers or less, since a maximum grain size is set to 50 micrometers or less, the diameter of average crystal grain will be controlled by this invention to 30 micrometers or less.

[0019] Next, control of the diameter of crystal grain by control of baking conditions is effective especially at the time of the rare earth oxide-alumina sintered compact which uses as a principal component $\text{Ln}_4\text{aluminum 2O9}$ which produces a martensitic transformation at the time of baking, and the compound which becomes LnAlO_3 . That is, for the rare earth oxide-alumina sintered compact which a combination presentation calcinates and by which it is compounded by this invention approach which mentioned above the mixture of the rare earth oxide and alumina which are $\text{Ln}_4\text{aluminum 2O9}$ or LnAlO_3 , since the diameter of crystal grain is controlled by 30 micrometers or less, the diameter of crystal grain is 100. When it was mum, the seen brittleness was not observed at all.

[0020] Although twin crystal does not generate that reason to the constituent particle in said sintered compact but a small number of twin crystal generates for the first time with progress of a crack, it is thought that it enlarges the reinforcement and the toughness of said sintered compact since this twin crystal absorbs the deformation energy of a crack and can absorb deformation energy also by motion of this twin plane. This is the device of toughening which is not known conventionally and is new discovery of artificers. According to an example, it explains below.

[0021]

[Example]

(Example 1) It is Ho 2O_3 in 50ml alcohol. 66g of powder, and aluminum 2O_3 9g of powder was put in, 1 moreml diethylamine was added, and wet blending was carried out for 48 hours using the ball mill. It heated at 60 degrees C after mixed termination, and alcohol was evaporated, subsequently to 5% of polyethylene-glycol water solution, it put in and mixed and this was dried. Then, $45 \times 20 \times 4 \text{ mm}^3$ It fabricated in the generation form of magnitude. Next, the temperature up was carried out to 500 ** with 2-degree-C programming rate for /in air, and by 500 **, this generation form was held for 1 hour, and carried out temporary quenching. The temperature up of this temporary-quenching sample was carried out to 1650 degrees C with 10-degree-C programming rate for /in air, it was held at 1650 degrees C for 4 hours, and the sintered compact was obtained.

[0022] The diameter of average crystal grain of the obtained sintered compact was 3 micrometers. Moreover, the flexural strength of a sintered compact was 600MPa(s), and was fracture toughness value $\text{KIC}=7 \text{ MP-m}^{1/2}$.

[0023] (Example 2) It is Nd 2O_3 in alcohol of 100 ml. Powder 115g and aluminum 2O_3 35g of powder was put in, 2 moreml diethylamine was added, and wet blending was carried out for 72 hours using the ball mill. It heated at 60 degrees C after mixed termination, and alcohol was evaporated, subsequently to 5% of polyethylene-glycol water solution, it put in and mixed and this was dried. Then, $45 \times 20 \times 4 \text{ mm}^3$ It fabricated in the generation form of magnitude. Next, it is in air about this generation form. The temperature up was carried out to 500 ** with 1.5-degree-C programming rate for /, by 500 **, it held for 1 hour and temporary quenching was carried out. The temperature up of this temporary-quenching sample was carried out to 1550 degrees C with 10-degree-C programming rate for /in air, it was held at 1550 degrees C for 2 hours, and NdAlO_3 sintered compact was obtained.

[0024] The diameter of average crystal grain of the obtained sintered compact was 3 micrometers. Moreover, the flexural strength of a sintered compact was 550MPa(s), and was fracture toughness value $\text{KIC}=7 \text{ MP-m}^{1/2}$.

[0025] (Example 3) They are 88.2g of 2OEr_3 powder, and aluminum 2O_3 in 70ml alcohol. 11.8g of powder was put in, 1 moreml diethylamine was added, and wet blending was carried out for 72 hours using the ball mill. It heated at 60 degrees C after mixed termination, and alcohol was evaporated, subsequently to 5% of polyethylene-glycol water solution, it put in and mixed and this was dried. Then, $45 \times 20 \times 4 \text{ mm}^3$ It fabricated in the generation form of magnitude. Next, the temperature up was carried out to 500 ** with 2-degree-C programming rate for /in air, and by 500 **, this generation form was held for 2 hours, and carried out temporary quenching. The temperature up of this temporary-quenching sample was carried out to 1530 degrees C with 15-degree-C programming rate for /in air, it was held at 1530 degrees C for 5 hours, and the sintered compact was obtained.

[0026] The diameter of average crystal grain of the obtained sintered compact was 5 micrometers or less. Moreover, the flexural strength of a sintered compact was 600MPa(s), and was fracture toughness value $\text{KIC}=8 \text{ MP-m}^{1/2}$.

[0027] (Example 4) They are 88.3g of 2OTm_3 powder, and aluminum 2O_3 in 70ml alcohol. 11.7g of powder was put in, 1 moreml diethylamine was added, and wet blending was carried out for 72 hours using the ball mill. It

heated at 60 degrees C after mixed termination, and alcohol was evaporated, subsequently to 5% of polyethylene-glycol water solution, it put in and mixed and this was dried. Then, 45x20x4mm³ It fabricated in the generation form of magnitude. Next, the temperature up of this generation form was carried out to 1600 degrees C with 2-degree-C programming rate for /in air, it was held at 1600 degrees C for 2 hours, and the sintered compact was obtained.

[0028] The diameter of average crystal grain of the obtained sintered compact was 5 micrometers. Moreover, the flexural strength of a sintered compact was 550MPa(s), and was fracture toughness value KIC=7 MP-m^{1/2}.

[0029] (Example 5) They are 76.2g of 2OLa₃ powder, and aluminum 2O₃ in 70ml alcohol. 23.8g of powder was put in, 1 moreml diethylamine was added, and wet blending was carried out for 72 hours using the ball mill. It heated at 60 degrees C after mixed termination, and alcohol was evaporated, subsequently to 5% of polyethylene-glycol water solution, it put in and mixed and this was dried. Then, 45x20x4mm³ It fabricated in the generation form of magnitude. Next, the temperature up was carried out to 500 ** with 2-degree-C programming rate for /in air, and by 500 **, this generation form was held for 2 hours, and carried out temporary quenching. The temperature up of this temporary-quenching sample was carried out to 1650 degrees C with 5-degree-C programming rate for /in air, it was held at 1650 degrees C for 2 hours, and the sintered compact was obtained.

[0030] The diameter of average crystal grain of the obtained sintered compact was 4 micrometers. Moreover, the flexural strength of a sintered compact was 600MPa(s), and was fracture toughness value KIC=6 MP-m^{1/2}.

[0031] (Example 6) They are 88.5g of 2OYb₃ powder, and aluminum 2O₃ in 80ml alcohol. 11.5g of powder was put in, 1 moreml diethylamine was added, and wet blending was carried out for 72 hours using the ball mill. It heated at 60 degrees C after mixed termination, and alcohol was evaporated, subsequently to 5% of polyethylene-glycol water solution, it put in and mixed and this was dried. Then, 45x20x4mm³ It fabricated in the generation form of magnitude. Next, the temperature up was carried out to 500 ** with 2-degree-C programming rate for /in air, and by 500 **, this generation form was held for 2 hours, and carried out temporary quenching. The temperature up of this temporary-quenching sample was carried out to 1600 degrees C with 10-degree-C programming rate for /in air, it was held at 1600 degrees C for 2 hours, and the sintered compact was obtained.

[0032] The diameter of average crystal grain of the obtained sintered compact was 3 micrometers. Moreover, the flexural strength of a sintered compact was 650MPa(s), and was fracture toughness value KIC=6.5 MP-m^{1/2}.

[0033] Thus, the rare earth oxide-alumina sintered compact obtained by the approach of this invention consists of particles of 30 micrometers or less of diameters of average crystal grain. And the sintered compact of this invention has sufficient reinforcement to present practical use and a fracture toughness value. Especially about a fracture toughness value, it has a mullite twice [about] the value of an alumina.

[0034]

[Effect of the Invention] As stated above, formation of pore can be prevented by controlling the diameter of crystal grain of a sintered compact to 30 micrometers or less according to this invention, and a uniform rare earth oxide-alumina sintered compact can be easily obtained on the organization target which has precise and high reinforcement and toughness. So, practical use can be conventionally presented with the rare earth oxide-alumina sintered compact with which practical use was not presented as a ceramic ingredient.

[0035] Therefore, according to this invention Engine components, a gas turbine aerofoil, the components for gas turbines, a corrosive equipment component, crucible, the components for ball mills, the heat exchanger for elevated-temperature furnaces and refractory material, the refractory material for altitude airframes, the combustion tube, the components for die casting, an insulating material, the charge of nuclear-fusion internal insulation, the charge of reactor material, a solar furnace ingredient, a tool, a thermal shield ingredient, What is effectively used in biomaterials, such as a base for electronic circuitries, a sealant, a joint and the components for bulbs, an artificial bone, and a dental implant, a dielectric material, a cutter and a cutter cutting edge, sporting goods, a pump, a nozzle, the magnetic head, a roller, a guide, bearing, a ferrule, and other large fields It can provide.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

 CLAIMS

[Claim(s)]

[Claim 1] The rare earth oxide-alumina sintered compact characterized by being a sintered compact (rare earth oxide 5 - 95wt% and alumina 95 - 5wt%), and the diameter of crystal grain of this sintered compact being 30 micrometers or less.

[Claim 2] The sintered compact according to claim 1 with which the above-mentioned rare earth oxide-alumina sintered compact uses Ln₄aluminum 2O₉ or LnAlO₃ (however, Ln rare earth elements and those mixture) as a principal component.

[Claim 3] The manufacture approach of the rare earth oxide-alumina sintered compact characterized by heating this mixture with the programming rate for 1 - 200 **/after that, and calcinating by fabricating the mixture of a rare earth oxide and an alumina and holding in a 1500-1800-degree C temperature region for 0.1 to 10 hours.

[Claim 4] The manufacture approach according to claim 3 that a rare earth oxide-alumina sintered compact is what uses Ln₄aluminum 2O₉ or LnAlO₃ (however, Ln rare earth elements and those mixture) as a principal component.

[Translation done.]

(19)日本国特許庁(J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開平5-85821

(43)公開日 平成5年(1993)4月6日

(51)Int.Cl.⁵

C 0 4 B 35/50
35/10

識別記号

庁内整理番号

7310-4G

E 8924-4G

F I

技術表示箇所

審査請求 未請求 請求項の数4(全 4 頁)

(21)出願番号 特願平3-273601

(22)出願日 平成3年(1991)9月26日

(71)出願人 000206048

大森 守

宮城県仙台市泉区高森1-1-42

(72)発明者 大森 守

宮城県仙台市太白区郡山6丁目5番8-205

(72)発明者 平井 敏雄

宮城県仙台市泉区高森3-4-91

(74)代理人 弁理士 小川 順三 (外1名)

(54)【発明の名称】 希土類酸化物-アルミナ焼結体およびその製造方法

(57)【要約】

【目的】 ボイドやボアなどの欠陥のない、高強度、高靱性で信頼性の高い希土類酸化物-アルミナ焼結体とその製造方法を提供する。

【構成】 希土類酸化物とアルミナを混合成形し、この生成形体を適性焼結温度および適性焼結時間にて焼結を施すことにより、該焼結体の結晶粒径を30 μ m以下に制御して、異常粒成長およびボアの発生を抑制し、もって強度ならびに靱性がともに優れた、実用に適する組織的に均一な希土類酸化物-アルミナ焼結体を容易に製造することができる。

【特許請求の範囲】

【請求項1】 希土類酸化物5～95wt%とアルミナ95～5wt%との焼結体であって、この焼結体の結晶粒径が30μm以下であることを特徴とする希土類酸化物-アルミナ焼結体。

【請求項2】 上記希土類酸化物-アルミナ焼結体が、 $\text{Ln}_4\text{Al}_2\text{O}_9$ もしくは LnAlO_3 （ただし、Lnは希土類元素およびそれらの混合物）を主成分とする請求項1に記載の焼結体。

【請求項3】 希土類酸化物とアルミナとの混合物を、成形し、その後、この混合物を1～200℃/分の昇温速度にて加熱し、1500～1800℃の温度域で0.1～10時間保持して焼成を行うことを特徴とする希土類酸化物-アルミナ焼結体の製造方法。

【請求項4】 希土類酸化物-アルミナ焼結体が、 $\text{Ln}_4\text{Al}_2\text{O}_9$ もしくは LnAlO_3 （ただし、Lnは希土類元素およびそれらの混合物）を主成分とするものである請求項3に記載の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、希土類酸化物-アルミナ焼結体およびその製造方法に関し、特に、強度や靱性低下の原因となるセラミックス中のポアを少なくし、異常粒成長を抑制することによって、高い強度ならびに靱性をもつ組織的に緻密な希土類酸化物-アルミナ焼結体について提案する。

【0002】

【従来の技術】酸化物系セラミックスは、高温での強度が高く、かつ耐熱性、耐酸化性および耐食性に優れているため、少なくともその融点の数百度以下の温度までは信頼して使用することができる。それ故に、融点が2000℃を超える希土類酸化物（希土類元素およびそれらの混合物の酸化物）やアルミナは、高温用セラミックス材料として有望視されていた。特に、この2種類の酸化物からなる混合セラミックスの場合も、その融点は2000℃近傍であり、いわゆる高温材料として有効なものと考えられている。

【0003】しかしながら、一般に、酸化物混合セラミックスについては、酸化物の混合物を焼成して焼結体を得る際、結晶粒が異常成長を引起し、100μm以上という大きな結晶粒となるために、ポアが形成されやすく緻密化されにくいという問題があった。しかも、得られる焼結体は、異常成長した結晶粒や前記ポアのために、強度、靱性ならびに硬度が著しく小さいものにしかならなかった。このような理由で、今日まで、このような酸化物混合セラミックスの焼結体は、実用に供されるまでに到らなかったのである。

【0004】特に、希土類酸化物が $\text{Ln}_4\text{Al}_2\text{O}_9$ や LnAlO_3 なる組成の化合物については、焼成の際に、マルテンサイト変態によって双晶を生成するために、非常に脆い多結

晶焼結体しか得ることができないという致命的な欠点があった。

【0005】

【発明が解決しようとする課題】ところで、上述した酸化物混合セラミックスの多結晶焼結体の異常粒成長を抑制する方法としては、従来、焼成温度と焼成時間とを制御する方法が有効であると漠然と考えられていた。しかし、希土類酸化物-アルミナ系の焼結体は、前記抑制技術が未だ確立されていないため、セラミックス材料として実用化されていないのが実情である。

【0006】本発明の目的は、反復可能性のある前記抑制技術を確立すること、即ち、酸化物混合セラミックスの多結晶焼結体について、その焼成温度と焼成時間の好適条件を究明し、このことによって該焼結体の結晶粒径を適性に制御し、もって強度ならびに靱性がともに優れた、実用に適する希土類酸化物-アルミナ焼結体およびその製造方法を提案することにある。

【0007】

【課題を解決するための手段】上掲の目的を実現するために鋭意研究した結果、発明者らは、希土類酸化物とアルミナとの混合物焼結体の結晶粒径を30μm以下に制御すると、この種の焼結体に望まれている所望の強度ならびに靱性が得られることを突き止めた。そこで、このような結晶粒径を得るための条件について、さらに研究を行ったところ、所定の配合割合の下で、焼成温度を1500～1800℃の範囲内とし、焼成時間を0.1～10時間とする焼成を行うことが有効であるとの知見を得、次のような要旨構成の本発明を完成した。

【0008】すなわち、本発明は、希土類酸化物5～95wt%とアルミナ95～5wt%との混合物を、成形し、その後、この混合物を1～200℃/分の昇温速度にて加熱し、1500～1800℃の温度域で0.1～10時間保持して焼成を行うことを特徴とする希土類酸化物-アルミナ焼結体の製造方法と、それによって合成される結晶粒径が30μm以下である希土類酸化物-アルミナ焼結体、ならびに、前記希土類酸化物-アルミナ焼結体が、 $\text{Ln}_4\text{Al}_2\text{O}_9$ もしくは LnAlO_3 を主成分とするものである希土類酸化物-アルミナ焼結体の製造方法と、それによって合成される結晶粒径が30μm以下である希土類酸化物-アルミナ焼結体である。

【0009】

【作用】発明者らの知見したところによれば、希土類酸化物-アルミナ焼結体は、その構成粒子の粒径を30μm以下に制御することが重要であり、このような結晶粒径の制御は、焼成条件を工夫することによって達成されることに気づいた。そこで、さらに研究を進めた結果、適正な両者の配合と、適正焼成温度ならびに適性焼成時間の焼結を施すことが、強度や靱性低下の原因となる焼結体中のポアや異常粒成長の防止に有効であることを見出し、本発明に想到した。

【0010】本発明の希土類酸化物-アルミナ焼結体の製造方法によれば、まず、希土類酸化物粉 5~95wt%とアルミナ粉95~5wt%とを混合する。

【0011】ここで、希土類酸化物粉が5wt%未満では、得られる希土類酸化物-アルミナ系焼結体の特性がアルミナ焼結体単独の特性に片寄ったものとなり、一方、アルミナが5wt%未満では、得られる希土類酸化物-アルミナ焼結体の特性が希土類酸化物単独の特性に片寄ったものとなるため、上記範囲に限定したのである。

【0012】なお、希土類酸化物 (Ln_2O_3) としては、例えば、 Sc_2O_3 , Y_2O_3 , La_2O_3 , CeO_2 , Pr_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 が好適に用いられる。

【0013】また、前記酸化物粉の混合に当っては、粉体の混合あるいは混練に用いられる通常の機械を使用することができる。この混合は、乾式、湿式のどちらでもよく、特に湿式の場合はエチルアミン、魚油等の表面活性剤を使用すると効果的に混合できる。

【0014】次に、上述のようにして得られた混合原料は一旦乾燥し、引焼き所定形状の生成形体に成形する。この成形工程では、成形助剤として有機高分子（ポリエチレングリコール、ポリビニルアルコール等）を上記混合原料に添加し、常法の既知成形技術を用いて成形することができる。

【0015】次に、前記生成形体は、1~200℃の昇温速度にて加熱し、1500~1800℃の温度に、0.1~10時間保持する焼成処理によって焼結体とする。この焼成温度が、1500℃より低いと、焼結が不十分になるために緻密な焼結体を得ることができず、一方1800℃より高いと結晶粒の異常成長を招く。このことから適性焼成温度の範囲は、1500~1800℃の範囲に限定される。次に、焼成時間は、前記焼成温度に関連し、焼成温度が低い時には長く、また高い時には短くすることが好ましいが、0.1時間より短いと焼結が不十分のために緻密な焼結体を得ることができず、一方、10時間超では結晶粒の異常成長を招くため、0.1~10時間の範囲に限定した。また、昇温速度は、1℃/分より遅いと焼結に時間がかかりすぎて経済的でなく、一方200℃/分より速いと緻密な焼結体を得られないため、1~200℃の範囲に限定される。

【0016】なお、焼成時の雰囲気としては、酸化雰囲気（例えば、窒素ガスやアルゴンガス、ヘリウムガス）でも良く、さらに真空中で焼成してもよい。

【0017】このような焼成条件を適用して得られた希土類酸化物-アルミナ系焼結体は、構成粒子の結晶粒径が30μm以下に制御される。その結果、従来では期待できなかった強度と靱性値を有する希土類酸化物-アルミナ焼結体を得ることができる。

【0018】一般にセラミックスは、構成粒子の結晶粒径が50μmを超えると、強度の低下が著しくなる。従っ

て、高強度のセラミックス材料を得るためには、粒径を50μm以下にしなければならない。それゆえに、本発明では、平均粒径を30μm以下にすると、最大粒径が50μm以下となることから、平均結晶粒径を30μm以下に制御しているのである。

【0019】次に、焼成条件の制御による結晶粒径の制御は、焼成時にマルテンサイト変態を生じる $\text{Ln}_3\text{Al}_2\text{O}_3$ および LnAlO_3 なる化合物を主成分とする希土類酸化物-アルミナ焼結体のときにとくに有効である。すなわち、配合組成が $\text{Ln}_3\text{Al}_2\text{O}_3$ あるいは LnAlO_3 である希土類酸化物とアルミナとの混合物を、上述した本発明方法によって焼成して合成される希土類酸化物-アルミナ焼結体は、結晶粒径が30μm以下に制御されているため、結晶粒径が100μmの場合に見られた脆さは全く観察されなかった。

【0020】その理由は、前記焼結体中の構成粒子に双晶が生成せず、クラックの進展に伴って初めて少ない数の双晶が生成するが、この双晶は、クラックの歪みのエネルギーを吸収し、かつ、この双晶面の動きによっても、歪みのエネルギーを吸収できるため、前記焼結体の強度と靱性を大きくすると考えられる。これは、従来知られていない強靱化の機構で、発明者らの新規の発見である。以下実施例に従って説明する。

【0021】

【実施例】

（実施例1）50mlのアルコール中に Ho_2O_3 粉66gと Al_2O_3 粉9gとを入れ、さらに1mlのジエチルアミンを添加し、ボールミルを用いて48時間湿式混合した。混合終了後、60℃に加熱して、アルコールを蒸発させ、次いで、5%のポリエチレングリコール水溶液に入れて混合し、これを乾燥した。その後、 $45 \times 20 \times 4 \text{ mm}^3$ の大きさの生成形体に成形した。次に、この生成形体を、空气中で2℃/分の昇温速度で500℃まで昇温し、500℃で1時間保持して仮焼した。この仮焼試料を、空气中で10℃/分の昇温速度で1650℃まで昇温し、1650℃に4時間保持して焼結体を得た。

【0022】得られた焼結体の平均結晶粒径は、3μmであった。また、焼結体の曲げ強度は600MPaであり、破壊靱性値 $K_{IC} = 7 \text{ MP} \cdot \text{m}^{1/2}$ であった。

【0023】（実施例2）100mlのアルコール中に Nd_2O_3 粉115gと Al_2O_3 粉35gとを入れ、さらに2mlのジエチルアミンを添加し、ボールミルを用いて72時間湿式混合した。混合終了後、60℃に加熱して、アルコールを蒸発させ、次いで、5%のポリエチレングリコール水溶液に入れて混合し、これを乾燥した。その後、 $45 \times 20 \times 4 \text{ mm}^3$ の大きさの生成形体に成形した。次に、この生成形体を、空气中で1.5℃/分の昇温速度で500℃まで昇温し、500℃で1時間保持して仮焼した。この仮焼試料を、空气中で10℃/分の昇温速度で1550℃まで昇温し、1550℃に2時間保持して NdAlO_3 焼結体を得た。

5

【0024】得られた焼結体の平均結晶粒径は、 $3\mu\text{m}$ であった。また、焼結体の曲げ強度は550MPaであり、破壊靱性値 $K_{IC}=7\text{MP}\cdot\text{m}^{1/2}$ であった。

【0025】(実施例3) 70mlのアルコール中に Er_2O_3 粉88.2gと Al_2O_3 粉11.8gとを入れ、さらに1mlのジエチルアミンを添加し、ボールミルを用いて72時間湿式混合した。混合終了後、60℃に加熱して、アルコールを蒸発させ、次いで、5%のポリエチレングリコール水溶液に入れて混合し、これを乾燥した。その後、 $45\times 20\times 4\text{mm}^3$ の大きさの生成形体に成形した。次に、この生成形体を、空气中で2℃/分の昇温速度で500℃まで昇温し、500℃で2時間保持して仮焼した。この仮焼試料を、空气中で15℃/分の昇温速度で1530℃まで昇温し、1530℃に5時間保持して焼結体を得た。

【0026】得られた焼結体の平均結晶粒径は、 $5\mu\text{m}$ 以下であった。また、焼結体の曲げ強度は600MPaであり、破壊靱性値 $K_{IC}=8\text{MP}\cdot\text{m}^{1/2}$ であった。

【0027】(実施例4) 70mlのアルコール中に Tm_2O_3 粉88.3gと Al_2O_3 粉11.7gとを入れ、さらに1mlのジエチルアミンを添加し、ボールミルを用いて72時間湿式混合した。混合終了後、60℃に加熱して、アルコールを蒸発させ、次いで、5%のポリエチレングリコール水溶液に入れて混合し、これを乾燥した。その後、 $45\times 20\times 4\text{mm}^3$ の大きさの生成形体に成形した。次に、この生成形体を、空气中で2℃/分の昇温速度で1600℃まで昇温し、1600℃で2時間保持して焼結体を得た。

【0028】得られた焼結体の平均結晶粒径は、 $5\mu\text{m}$ であった。また、焼結体の曲げ強度は550MPaであり、破壊靱性値 $K_{IC}=7\text{MP}\cdot\text{m}^{1/2}$ であった。

【0029】(実施例5) 70mlのアルコール中に La_2O_3 粉76.2gと Al_2O_3 粉23.8gとを入れ、さらに1mlのジエチルアミンを添加し、ボールミルを用いて72時間湿式混合した。混合終了後、60℃に加熱して、アルコールを蒸発させ、次いで、5%のポリエチレングリコール水溶液に入れて混合し、これを乾燥した。その後、 $45\times 20\times 4\text{mm}^3$ の大きさの生成形体に成形した。次に、この生成形体を、空气中で2℃/分の昇温速度で500℃まで昇温し、500℃で2時間保持して仮焼した。この仮焼試料を、空气中で5℃/分の昇温速度で1650℃まで昇温し、1650℃に2時間保持して焼結体を得た。

【0030】得られた焼結体の平均結晶粒径は、 $4\mu\text{m}$

6

であった。また、焼結体の曲げ強度は600MPaであり、破壊靱性値 $K_{IC}=6\text{MP}\cdot\text{m}^{1/2}$ であった。

【0031】(実施例6) 80mlのアルコール中に Yb_2O_3 粉88.5gと Al_2O_3 粉11.5gとを入れ、さらに1mlのジエチルアミンを添加し、ボールミルを用いて72時間湿式混合した。混合終了後、60℃に加熱して、アルコールを蒸発させ、次いで、5%のポリエチレングリコール水溶液に入れて混合し、これを乾燥した。その後、 $45\times 20\times 4\text{mm}^3$ の大きさの生成形体に成形した。次に、この生成形体を、空气中で2℃/分の昇温速度で500℃まで昇温し、500℃で2時間保持して仮焼した。この仮焼試料を、空气中で10℃/分の昇温速度で1600℃まで昇温し、1600℃に2時間保持して焼結体を得た。

【0032】得られた焼結体の平均結晶粒径は、 $3\mu\text{m}$ であった。また、焼結体の曲げ強度は650MPaであり、破壊靱性値 $K_{IC}=6.5\text{MP}\cdot\text{m}^{1/2}$ であった。

【0033】このように本発明の方法で得られた希土類酸化物-アルミナ焼結体は、平均結晶粒径 $30\mu\text{m}$ 以下の粒子で構成されている。しかも、本発明の焼結体は、実用に供されるに十分な強度ならびに破壊靱性値を有する。特に破壊靱性値に関しては、アルミナやムライトの約2倍の値を有する。

【0034】

【発明の効果】以上述べたように本発明によれば、焼結体の結晶粒径を $30\mu\text{m}$ 以下に制御することにより、ポアの形成を阻止し、緻密で高い強度と靱性を有する組織的に均一な希土類酸化物-アルミナ焼結体を容易に得ることができる。それ故に、従来、セラミックス材料として実用に供されなかった希土類酸化物-アルミナ焼結体を実用に供することができる。

【0035】従って、本発明によれば、エンジン部品、ガスタービン翼、ガスタービン用部品、腐食性装置部品、増埧、ボールミル用部品、高温炉用熱交換器および耐火材、高空飛翔体用耐火材、燃焼管、ダイカスト用部品、絶縁材料、核融合炉材料、原子炉用材料、太陽炉材料、工具、熱遮蔽材料、電子回路用基体、シール材、継手やバルブ用部品、人工骨や人工歯根等の生体材料、誘電材料、刃物やカッター刃、スポーツ用品、ポンプ、ノズル、磁気ヘッド、ローラー、ガイド、軸受、フェール、その他の広い分野で有効に用いられるものを提供できる。

THIS PAGE BLANK (USPTO)